

How Do SAMs Grow?

There is a growing interest in creating self-assembled monolayers (SAMs) of organic materials in standard environments. The best-suited method to investigate their formation is to measure *in situ* x-ray reflectivity curves during the SAM growth, which provide rich information on all of the important structural parameters. We have successfully studied octadecyltrichlorosilane (OTS) SAMs absorbed onto silicon (Si) using this method and found that they grow by formation of well ordered islands that follow a simple Langmuir model.

For the last 15 years or so, a complementary technique to the technologically important field of inorganic thin films has been developing: organic thin films. The subject of several popular science articles [1], the formation of organic thin films using the self-assembly (SA) technique has been increasingly explored. This technique, when applied to the area of thin films, refers to the spontaneous formation of an ordered monolayer of organic molecules on a surface. The benefits of using organic rather than inorganic materials are two-fold: one, an innumerable number of molecules can be synthesized that have an extremely wide variety of functionality; and two, molecules can be created that deposit onto a substrate in a self-limiting manner, so that only one monolayer of the molecules is deposited at each step. This level of control of both the functionality and the structure of a film is difficult for inorganic techniques, requiring large amounts of capital to build cleanrooms and ultra-high-vacuum systems. Comparatively, chemists can much more easily create self-assembled monolayers (SAMs) of organic materials in standard environments.

While research on SAMs has proceeded briskly, much remains to be learned. One of the fundamental questions is “How do SAMs grow?” Several things complicate research into this area. First, while SAMs can be grown in vacuum chambers using vapors of organic molecules [2], the most common and expedient method is to grow SAMs from solution. Most characterization methods are much less suited to studying liquid-solid interfaces

than air-solid interfaces because the probe has to penetrate the intervening liquid. Additionally, SAMs are, by definition, single monolayers of molecules, typically with thicknesses on the order of 20-50 Å; very few methods exist for accurately determining the structure of such a length scale.

One of the best methods for studying ultra-thin films is x-ray reflectivity (XRR) [3]. Because x-rays coherently scatter and have wavelengths that are similar to the thickness of a monolayer, they can be used as a high-resolution structural probe. X-rays that are shone onto a sample at some incident angle will be reflected off the different interfaces in a film and will interfere with each other, creating a characteristic interference pattern as a function of the incident angle. The period of the interference is determined by the film thickness. The amplitude of the interference oscillations is related to the difference in electron density at each of the interfaces. Finally, interfaces are not completely abrupt, and any amount of width at an interface reduces the amount of x-rays that are reflected at the specular angle. Therefore, by looking at a reflectivity curve, all of the important structural parameters—thickness, electron density, and interfacial width—of a film can be obtained.

The presence of the solution can be mitigated by the use of synchrotron x-rays. A synchrotron source is bright enough that, despite the loss of intensity from passing through the liquid, enough photons remain. Furthermore, the energy of the x-rays can be set to a moderately high value, since the

higher the energy, the less the x-rays interact with matter, and less intensity is lost in the solution. The choice of a good, low-density solvent will also reduce absorption.

We have performed the first *in situ* (while in solution) XRR study of the formation of a SAM, using octadecyltrichlorosilane (OTS) absorbed onto silicon (Si). The OTS/Si SAMs have been very widely studied, perhaps only second to another important system, alkylthiols on gold substrates. Since OTS molecules interact strongly with each other (they bind both to the substrate and to nearest neighbors via Si-O bonds), the OTS/Si SAM may not be a good model for all types of SAMs. However, they are a very important class of SAMs, and some information learned about their film formation should be of interest in relation to other systems.

We have also performed *ex situ* “interrupted growth” studies in order to elucidate the differences between these kinds of experiments and to determine the role of the solvent in film formation beyond just supplying molecules to the surface. In these experiments, growth is stopped by removing the substrates from solution before complete films have had time to form. The films are then characterized outside of the growth environment.

The generally accepted mode of growth for OTS and related SAMs is “island” growth, in which the molecules arrange themselves into compact collections on the surface, with coverage increasing by island growth and nucleation of new islands [4]. However, various groups performing *ex situ* growth experiments have also seen the “uniform” growth mode. At low coverage, the molecules tilt over, standing up as the coverage increases to make room for additional molecules at the substrate surface [5]. Figure 1 schematically shows these growth modes. Other modes are possible and have been seen in various experiments [6]. All of the previous experiments on OTS/Si that examined the structural evolution of the films during growth have been performed *ex situ*, and it might be expected that the drastic change in the local environment the film experiences between growth and measurement could affect the results. *In situ* experiments should more

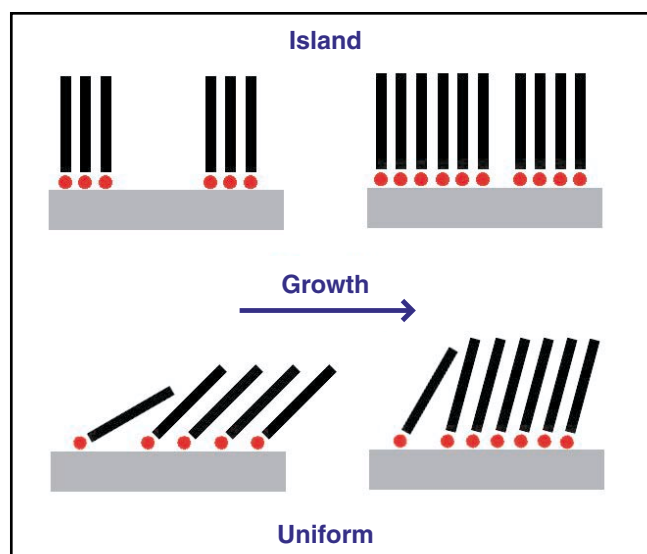


FIG. 1. A schematic representation of two possible monolayer growth modes. The top shows island growth, in which the molecules form dense islands of (nearly) vertical molecules. Additional molecules attach at island edges or form new islands as the coverage increases. The bottom shows “uniform” growth, in which molecules deposit randomly on the substrate, falling over at low coverage. As more molecules adsorb on the surface, the molecules begin to stand up.

readily show the actual growth mode.

Our *in situ* experiments were performed using solutions of OTS in heptane with a variety of concentrations. At normal concentrations, complete films are formed on the order of 1-2 hrs. Since XRR measurements take 20 min to 1 hr, such concentrations are not accessible. We therefore limited ourselves to relatively low concentrations, on the order of $1\ \mu\text{M}$. Some of our results are shown in Fig. 2. There are two clear effects. The thickness of the film is always $\sim 25\ \text{\AA}$, which is the thickness of a complete film; and the density of the film increases during growth. This is in complete opposition to the uniform growth mode (found using *ex situ* XRR). When including the fact that the film surface roughness is relatively constant (no evidence is found for a large-scale change in this parameter), we find that the growth mode is via island growth.

In contrast, our *ex situ* experiments show a different growth mode. Films outside of solution, even those that we had just studied *in situ* and had been found to have full thickness and a normal density, have a decreased thickness and density.

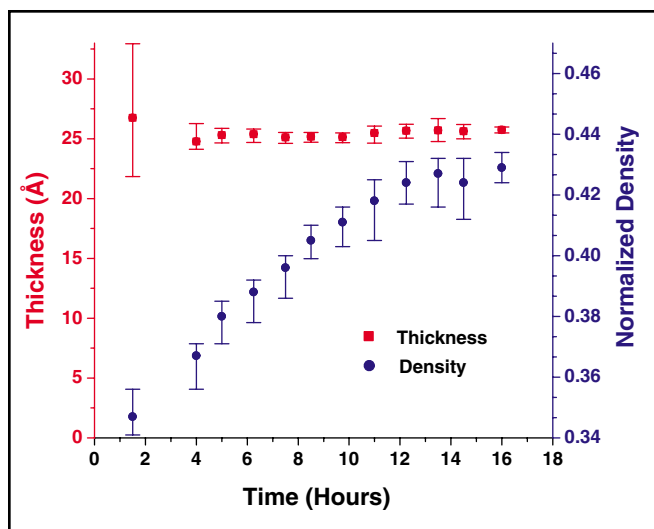


FIG. 2. The results of the in situ XRR experiment. The film thickness is found to be about 25 Å at all times, which is approximately the length of the molecules. The film density is found to increase over time. Including the fact that the surface roughness does not radically change during growth (not shown), the growth mode is determined to be via island formation. (Taken from A. G. Richter et al., *Langmuir* **14**, 5980 [1998]).

Modeling also shows that the molecules have a wide range of tilts. These results do not exactly match with the uniform growth mode but are quite similar. Since the molecules are vertical when in solution, it must be the removal from solution (and drying) that causes the molecules to fall over. This effect presumably accounts for the fact that some groups displayed uniform growth. The variety of morphologies that we obtained for *ex situ* films also suggests why there are different results seen when relying on the interrupted growth technique.

We can calculate the film coverage (0 when there is no film, 1 when the film is complete) as a function of time and fit the resulting curve to a growth model. The simplest model is Langmuir, which treats the molecules as noninteracting. The functional form involves an exponential with a characteristic time constant τ . While this simple model would seem to be in direct contrast to the fact that OTS molecules bond to each other and seem to interact enough to form compact islands, the simple Langmuir form is also arrived at for a wide range of growth models in certain limits. When we applied this model to our coverage curves, we find good

agreement except at very early times for the lowest concentration solutions, with τ on the order of 1 to 6 hours, depending on the concentration (see Fig. 3).

Our results for OTS/Si are quite similar to those found by others using different characterization techniques and systems. In particular, one group examined octadecylphosphonic acid (OPA) on mica using atomic-force microscopy and found Langmuir growth with a similar growth rate, though at a much higher solution concentration [7]. Interestingly, OPA does not interact strongly with its neighbors (or with mica), so the similar growth model and rate suggests that OTS may not either, at least not until much later in the growth process.

In conclusion, we have found evidence that OTS grows by formation of well-ordered islands. The growth follows a simple Langmuir model, suggesting that perhaps the molecules do not fully cross-link until late in the film formation process. We have also found that the solvent and not yet completely bound OTS molecules keep the molecules vertical while in solution; upon drying, the molecules fall over, assuming a range of tilts. This work, while helping to elucidate the actual growth mode for an important type of SAM, also illustrates

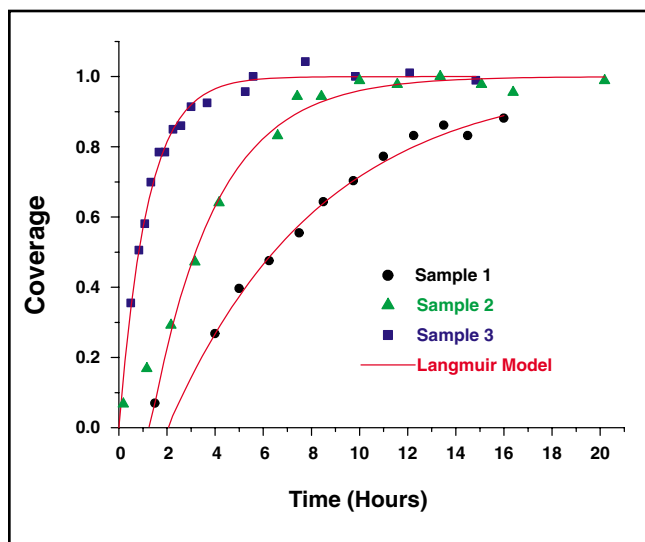


FIG. 3. Growth curves for three of the samples and fits to a Langmuir growth model. Sample 1 and Sample 2 have the same solution low concentration, and both show a deviation from Langmuir growth at early times. Sample 3 was grown using a higher concentration and shows no "time-offset" and a faster growth rate. (Taken from A. G. Richter et al., *Phys. Rev. E* **61**, 607 [2000]).

the need for characterizing growth while *in situ* to obtain consistent and reliable results.

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